



Mechanical behavior of Li-ion-conducting crystalline oxide-based solid electrolytes: a brief review

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Abstract

Li-ion-conducting solid electrolytes are receiving considerable attention for use in advanced batteries. These electrolytes would enable use of a Li metal anode, allowing for batteries with higher energy densities and enhanced safety compared to current Li-ion systems. One important aspect of these electrolytes that has been overlooked is their mechanical properties. Mechanical properties will play a large role in the processing, assembly, and operation of battery cells. Hence, this paper reviews the elastic, plastic, and fracture properties of crystalline oxide-based Li-ion solid electrolytes for three different crystal structures: $\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}$ (garnet) [LLZO], $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ (perovskite) [LLTO], and $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (NaSICON) [LATP]. The experimental Young's modulus value for (1) LLTO is ~ 200 GPa, (2) LLZO is ~ 150 GPa, and (3) for LATP ~ 115 GPa. The experimental values are in good agreement with density functional theory predictions. The fracture toughness value for all three of LLTO, LLZO, and LATP is approximately 1 MPa m^{-2} . This low value is expected since, they all exhibit at least some degree of covalent bonding, which limits dislocation mobility leading to brittle behavior.

Keywords Solid electrolyte · Li-conductor · Young's modulus · Hardness · Fracture toughness

Introduction

Many new battery chemistries based on the use of a metallic Li anode are under consideration in order to increase the energy density over the presently used Li-ion batteries. These include aqueous Li-air and all solid-state batteries. These batteries require a solid Li-ion-conducting electrolyte. The major requirements for the solid Li-ion-conducting electrolyte are high Li-ion conductivity, low electronic conductivity, and chemical/electrochemical stability with the Li anode/cathodes [1–5]. In many applications, the solid electrolyte may also be required to exhibit adequate mechanical properties. These include the elastic, plastic, and fracture properties of the solid electrolyte. A scenario where elastic properties are important was described by Monroe and Newman [5]. Using

the linear elasticity theory, it was shown that to prevent the initiation of dendrites during charging at the Li electrode/solid electrolyte interface, the shear modulus of the Li-ion-conducting solid electrolyte must be greater than twice the shear modulus of Li. Regarding fracture properties, it has been recently suggested that the critical current (maximum current above which Li dendrite formation occurs) during charging is dependent on the fracture stress (higher fracture stress, higher critical current) of the Li-ion-conducting solid electrolyte [6]. At present, information on the mechanical properties of solid Li-ion conductors is limited. Thus, it is the purpose of this paper to present a short summary of the recent work on the elastic, plastic, and fracture properties of crystalline oxide-based Li-ion solid electrolytes for three different crystal structures (garnet, perovskite, and NaSICON).

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Discussion

Elastic properties (Young's modulus)

Young's modulus, E , is a measure of the stiffness of a solid material. It is an elastic property which depends on the bonding and crystal structure of the solid. It is independent of microstructure (e.g., grain size).

The Young's modulus for $\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}$ (garnet) [7, 8], $\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.5}\text{Zr}_{1.5}\text{O}_{12}$ (garnet) [8], $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ (perovskite) [9–11], $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (NaSICON) [12] is listed in Table 1. Also shown in Table 1 is the technique used to determine E . From Table 1, several important points are noted. Firstly, it can be observed that E for $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [LLTO] ~ 200 GPa, for $\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}/\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.5}\text{Zr}_{1.5}\text{O}_{12}$ [LLZO] ~ 150 GPa, and for $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [LATP] ~ 115 GPa. LLTO has the highest E value, while LATP has the lowest value. The experimental E values can be compared to theoretical values predicted using density functional theory (DFT). DFT predicts ~ 234 GPa for $\text{Li}_{0.13}\text{La}_{0.63}\text{TiO}_3$ [13], ~ 150 GPa for $\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}/\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.5}\text{Zr}_{1.5}\text{O}_{12}$ [8], and ~ 143 GPa for $\text{LiTi}_2(\text{PO}_4)_3$ [13]. The DFT values are in close agreement with the experimental values and exhibit the same trend, in that LLTO has the highest E value while LATP has the lowest value. Secondly, the values determined using acoustic impulse excitation are in good agreement with those determined by nanoindentation. Acoustic impulse excitation gives information on bulk polycrystalline elastic properties whereas, nanoindentation examines single grains within the sample.

LLTO and LATP are not stable with metallic Li since, they contain Ti^{+4} which will be reduced to Ti^{+3} when in contact with Li, leading to undesirable electronic conduction. Therefore, we focus the remainder of our elastic properties discussion on LLZO, which does not contain redox-active species. The E value for LLZO can be used to estimate its shear modulus, G , from which LLZO's resistance to Li dendrite nucleation during cycling can be predicted. As previously mentioned, the perturbation analysis of Monroe and Newman [5] suggested to prevent dendrite nucleation that the shear modulus of a solid lithium-conducting electrolyte should be at least twice that of Li metal. To assess whether this criterion is met for LLZO, Young's modulus for LLZO must be converted to a shear modulus. In an isotropic elastic solid, the shear modulus is related to Young's modulus and Poisson's ratio, ν , through the following relation [8]:

$$G = \frac{E}{2(1 + \nu)} \quad (1)$$

A Poisson's ratio of 0.26 determined using resonant ultrasound spectroscopy for LLZO was used in the present calculations [7]. From Eq. (1), the predicted shear modulus value for LLZO is ~ 60 GPa. The shear modulus value for Li is ~ 5 GPa [8]. Since the shear modulus of LLZO (~ 60 GPa) exceeds the critical shear modulus criterion (~ 10 GPa), no Li dendrite nucleation is expected. However, dendrite formation has been observed in LLZO at current densities > 0.5 mA cm^{-2} [14–18]. It has been recently observed that Li preferentially deposits along LLZO grain boundaries [19].

Thus, if the stability criterion of Monroe and Newman [5] is correct, then based on the above result, it may be more appropriate to consider the shear modulus for the grain boundary, G_{GB} , and not the polycrystalline value listed in Table 1 to determine if dendrites will form. It has been suggested that because of the large excess volume associated with a grain boundary, E_{GB} can have values ranging from ~ 0.6 to 0.2 of the E values listed in Table 1 [20]. This results in G_{GB} values ranging from 36 to 12 GPa. Since the lower end value (~ 12 GPa) is close to the stability threshold [5] (~ 10 GPa), it is possible that the Monroe-Newman criterion is still valid when interpreted in this manner; however, more work on the mechanical properties of grain boundaries in LLZO is needed to verify this.

In addition to the shear modulus, the value of E can be used to predict the fracture stress, σ_f ,

$$\sigma_f = (E\gamma/\pi a)^{1/2} \quad (2)$$

where γ is the energy for fracture and a is the critical flaw size, if γ and a are known. It can also be used to predict fracture toughness, K_{c} , if γ is known [21, 22].

$$K_{\text{c}} = (E\gamma)^{1/2} \quad (3)$$

Conversely, knowing the value of E and the fracture stress or fracture toughness and the critical flaw size allows for determination of the energy for fracture.

Plastic properties (hardness)

Hardness, H , is usually defined as resistance to deformation. It is a plastic property which depends on the bonding, crystal structure, and microstructure (e.g., grain size). Nanoindentation/microindentation hardness is a useful probe for the strength of a brittle material because the indentation stress field has a significant compressive hydrostatic component which reduces the chance for fracture, by preventing crack propagation and hence, allows the material to deform plastically.

The nanoindentation or microindentation hardness values for LLZO [28], LLTO [9, 11, 27], and LATP [9] are listed in Table 2, along with associated microstructural variables. For the case of nanoindentation, loads typically range from 1 to 500 μN with indent impressions ~ 1 μm or less [23, 24]. For the case of microindentation measured using a Vickers indenter, loads typically range from 1 to 10 N with indent impressions as large as 20 μm [25, 26]. The hardness values for the nanoindentation measurements were taken where the hardness was independent of depth and for the case of the microhardness measurements where the hardness was independent of load. Nanoindentation has the capability to examine single grains within the sample, while microindentation usually

Table 1 Elastic modulus (E)

Material	Technique	Sample grain size (μm)	Sample relative density (%)	E (GPa)
$\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}$ [7]	RUS	5	97	150 ± 0.4
$\text{Li}_{6.19}\text{Al}_{0.28}\text{La}_3\text{Zr}_2\text{O}_{12}$ [8]	Nano Impulse	5–50	99	150 ± 2.2 146 ± 0.8
$\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ [8]	Nano Impulse	1–10	99	140 ± 2.1 154 ± 2.7
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [9]	Nano	0.8	97	200 ± 3
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [10]	Impulse	2.4	99	223
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	Impulse	1.5	95	143
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	Impulse	2.5	99	199
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	Impulse	13	99	203
$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [12]	Stress-Strain	1.7	96	115

RUS resonant ultrasound spectroscopy, Nano nanoindentation, Impulse acoustic impulse excitation, Stress-Strain slope of stress-strain curve

samples several grains in a polycrystalline material and thus, can be a function of grain size. It is well known that hardness tends to increase as grain size decreases [21, 22]. From Table 2, it is observed that the Vickers hardness values for LLTO range from 8.1 to 9.5 GPa [9, 11, 27]. For all LLTO samples listed in Table 2, there is no significant difference in relative density and four out of the five samples exhibit a similar grain size. Thus, it would be expected that these four samples would exhibit similar hardness values. Indeed, three out of the four do have similar values close to 9.5 GPa. The fourth sample has a lower value of 8.1 GPa. At present, the reasons for this low value are not known. The hardness value for LLZO determined by nanoindentation and microhardness measurements is ~ 9.1 GPa [28]. For LATP with a nanoscale grain size (300 nm), the hardness determined by nanoindentation is ~ 7.1 GPa.

Hardness values can also be used to determine the nature of atomic bonding. Gilman [29] and Chin [30] reported that the ratio of the hardness to the shear modulus for crystals is relatively constant for different types of bonding: For covalent,

ionic, and metallic bonding, $H/G \sim 0.1$, $H/G \sim 0.01$, and $H/G \sim 0.006$, respectively [29, 30]. The modulus (Table 1) and hardness (Table 2) data can be used to calculate the Gilman-Chin parameter (H/G) for LLTO, LLZO, and LATP to determine their dominant bonding type. The shear modulus was estimated using data from Table 1 and Eq. (1) with $\nu = 0.26$. The H/G values for LLZO, LATP, and LLTO are ~ 0.12 , 0.11 , and 0.15 , respectively. The H/G values for LLTO, LLZO, and LATP are similar, suggesting that they all exhibit similar, covalent bonding according to the Gilman-Chin metric. This result is in agreement with DFT predictions [9].

Fracture properties (fracture toughness)

Fracture toughness is the ability of a material containing a crack to resist fracture. It depends on bonding, crystal structure, and microstructure [21, 22, 31]. It is an important property for solid-state electrolytes since, it represents resistance to rapid fracture that could occur during cell assembly or battery operation.

Table 2 Hardness (H)

Material	Technique	Sample grain size (μm)	Sample relative density (%)	H (GPa)
$\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}$ [28]	Nano/micro	4	98	9.1 ± 0.53
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [9]	Micro	0.8	97	9.5 ± 0.72
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [27]	Micro	1.5	94	9.4 ± 0.84
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	Micro	1.5	95	8.1 ± 0.75
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	Micro	2.5	99	9.5 ± 0.63
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	Micro	13	99	8.4 ± 0.48
$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [9]	Nano	0.3	99	7.1 ± 0.44

Nano nanoindentation (Berkovich indenter), Micro microindentation (Vickers indenter)

Fracture toughness values for LLZO [28, 32], LLTO [9, 11], and LATP [12] are listed in Table 3. Also shown in Table 3 are the techniques (indentation or single edge notched bending) used to determine K_c and the microstructural properties (grain size and relative density). From Table 3, several important points are noted. Firstly, all K_c values are $\sim 1 \text{ MPa m}^{-2}$. Secondly, for LLTO, similar K_c values were exhibited using the indentation and single edge notch bending methods.

In general, ceramics exhibit fracture toughness values from ~ 0.5 to 5 MPa m^{-2} , with values between ~ 0.5 and 2 MPa m^{-2} for single crystals and for polycrystals between ~ 2 and 5 MPa m^{-2} [21, 22, 31]. In contrast, metals exhibit much higher fracture toughness values, with values between ~ 20 to 100 MPa m^{-2} [33]. The K_c values for LLZO, LLTO, and LATP are near the low end of single crystal values. This observation suggests LLZO, LLTO, and LATP are extremely brittle, similar to glass. This is expected, since they all exhibit covalent bonding, which results in a high Peierls stress that limits dislocation mobility and hence, reduced plastic deformation at room temperature, leading to brittle behavior.

It has been recently suggested that the nucleation of Li dendrites is a function of the grain boundary (ionic) conductivity and fracture stress of the Li-ion-conducting solid electrolyte [6]. The higher the grain boundary conductivity and fracture stress, the higher the critical current (the current at which dendrite nucleation occurs). The fracture stress can be calculated from fracture toughness data using the equation [21, 22]:

$$\sigma_f = K_c (\pi a_c)^{-1/2} \quad (4)$$

The critical flaw size for LLZO, a_c , is the largest microstructural parameter, either the pore or grain size [31, 34]. Microscopic examination of hot-pressed LLZO samples revealed that all pores had sizes less than the grain size of $\sim 4 \mu\text{m}$. Thus, a_c in Eq. (4) is set to $4 \mu\text{m}$ (grain size) for LLZO. Inserting this value into Eq. (4) with $K_c = 1 \text{ MPa m}^{-2}$, yields $\sigma_f \sim 280 \text{ MPa}$. No experimental fracture stress data exists for LLZO to compare to this prediction. However, the predicted value can be compared to the fracture stress value for another oxide with the garnet structure, $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG). The measured fracture stress of polycrystalline YAG of similar relative density and grain size is $\sim 290 \text{ MPa}$ [35]. This value is in excellent agreement with the predicted value for LLZO. The fracture stress for LLTO ranges from 150 to 250 MPa [10, 11], while that for LATP is around 150 MPa [12].

The low fracture toughness of LLZO, LLTO, and LATP needs to be increased without a decrease in ionic conductivity. One possible solution is to form a composite mixture by adding a second phase which has a different thermal expansion coefficient and elastic modulus than the matrix. This approach has been used to increase not only the fracture

toughness but also the fracture strength of Na-ion-conducting beta-alumina through the incorporation of a second phase, ZrO_2 ($\sim 15 \text{ vol}\%$), into the beta-alumina matrix [36]. It was observed that the addition of ZrO_2 increased the fracture strength by 50% , from 200 to 300 MPa , and doubled the fracture toughness, from 2 to 4 MPa m^{-2} [36]. The improvement in strength/toughness was attributed to grain size refinement and crack deflection/branching [36].

Adopting this strategy, the addition of ZrO_2 ($10 \text{ vol}\%$) to LLZO was attempted as a means to increase its fracture toughness. After heat treatment at 1 h at $1100 \text{ }^\circ\text{C}$, X-ray diffraction of the ZrO_2/LLZO mixture revealed that the following reaction occurred: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} + \text{ZrO}_2 \rightarrow \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} + \text{ZrO}_2 + \text{La}_2\text{Zr}_2\text{O}_7 + \text{Li}_2\text{ZrO}_3$. A significant amount of LLZO had reacted with zirconia to form pyrochlore ($\text{La}_2\text{Zr}_2\text{O}_7$) and lithium zirconate (Li_2ZrO_3). Attempts to add other oxides such as Al_2O_3 or YAG to LLZO also revealed a significant reaction had occurred between these second phase oxides and LLZO to form pyrochlore and lithium zirconate. In addition, it was observed that after heat treatment at 1 h at $1100 \text{ }^\circ\text{C}$, the addition of second phase SiC or Si_3N_4 ($\sim 10 \text{ vol}\%$) had reacted with LLZO to also form a significant amount of pyrochlore. For the case of Si_3N_4 , the majority phase remaining after heat treatment was pyrochlore and not LLZO.

Another attempt to increase the fracture toughness of LLZO was undertaken by manipulation of the microstructure. The two major microstructural variables for a single-phase material are grain size and porosity. It has been shown that changing the grain size in the micron grain size region for a cubic material will not lead to an increase in fracture toughness [37, 38]. Thus, it was decided to vary the porosity by varying the relative density and observe its effect on fracture toughness. It was observed for LLZO with a relative density $\sim 98\%$ that $K_c \sim 1 \text{ MPa m}^{-2}$. As the relative density decreased to $\sim 85\%$, K_c more than doubled to a value $\sim 2.4 \text{ MPa m}^{-2}$. The grain size remained about the same for these two relative densities. The fracture mode changed from almost entirely transgranular at 98% relative density to almost completely intergranular at 85% relative density. The increase in fracture toughness and change in fracture mode as relative density decreased was a result of the increased porosity along grain boundaries, which lead to weakening of the grain boundaries promoting a crack deflection toughening mechanism [28]. However, it was observed that as the fracture toughness increased, the total ionic conductivity decreased by a factor of about 30 , mainly as a result of the increase in grain boundary resistance [28].

Another possible solution could be the addition of a high Li-ion conductivity second phase (e.g., glass) along the LLZO grain boundaries that allows for high Li-ion conductivity across the grain boundaries but, when subjected to a mechanical stress, would preferentially fracture along the grain boundaries giving improved toughness.

Table 3 Fracture toughness (K_{IC})

Material	Technique	Sample grain size (μm)	Sample relative density (%)	K_{IC} (MPa m^{-2})
$\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}$ [33]	Indentation	5	97	1.25 ± 0.32
$\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}$ [28]	Indentation	4	98	0.97 ± 0.11
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [9]	Indentation	0.8	97	1 ± 0.42
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	SENB	1.5	95	1.15 ± 0.11
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	SENB	2.5	99	1.18 ± 0.09
$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [11]	SENB	13	99	1.24 ± 0.12
$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [12]	SENB	1.7	96	1.1 ± 0.30

For indentation, Vickers indenter was used

SENB single edge notch bending

Summary

This paper presents a brief review of the elastic, plastic, and fracture toughness properties of three crystalline oxide-based Li-ion-conducting solid electrolytes: (1) $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ [LLTO], (2) $\text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12}/\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.5}\text{Zr}_{1.5}\text{O}_{12}$ [LLZO], and (3) $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [LATP]. The most important observations are summarized as follows:

1. The experimental Young's modulus, E , for (1) LLTO is ~ 200 GPa, (2) LLZO is ~ 150 GPa, and (3) LATP is ~ 115 GPa. The experimental values are in good agreement with density functional theory predictions. The shear modulus of LLZO is sufficient to prevent Li dendrite nucleation according to the stability criterion of Monroe and Newman [5]. However, recent experimental findings (showing dendrite penetration along grain boundaries) suggest that this criterion should be modified to reflect the moduli of the grain boundaries, which could be significantly softer than the bulk.
2. The hardness value, H , for (1) LLTO ~ 9.5 GPa, (2) LLZO ~ 9.1 GPa, and (3) LATP ~ 7.1 GPa. The ratio H/G for LLTO, LLZO, and LATP was similar, suggesting that they all have the same type of dominant bonding: covalent bonding. This result is in agreement with DFT predictions.
3. The fracture toughness, K_{IC} , for LLTO, LLZO, and LATP are all approximately 1 MPa m^{-2} . This value suggests LLZO, LLTO, and LATP are extremely brittle. This is expected since they all exhibit covalent bonding, which results in a high Peierls stress that limits dislocation mobility and hence, plastic deformation at room temperature. Attempts to increase the K_{IC} of LLZO through the addition of second phase oxide/carbide/nitride particles were unsuccessful due to chemical reactivity issues. The fracture stress for LLTO, LLZO, and LATP ranges from ~ 150 to 300 MPa.

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